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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Diacylamino-Dihalogeno-1,4-Benzoquinones and a process for their manufacture

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Postfach, 4000 Basle 7, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that the 2,5-dialkanoylamino-3,6-di-halogeno-1,4-benzoquinones, which are of importance in the manufacture of dioxazine pigments of high fastness, are obtained in good yields by acylating a 2,5-diamino-3,6-dihalogeno-1,4-benzoquinone. Only those 2,5-diacylamino - 3,6 - dihalogeno - 1,4 - benzoquinones which are derived from lower aliphatic or cycloaliphatic monocarboxylic acids can be prepared by this process. The process referred to is unsuitable for the manufacture of 2,5-diaroylamino - 3,6 - dihalogeno - 1,4 - benzoquinones. For the manufacture of these compounds it has so far been necessary to employ a complicated multi-stage process starting from quinone (see French Specification No. 1,345,524). Since the aforementioned diaroylamino - dihalogeno - benzoquinones are valuable starting materials for the manufacture of very fast dioxazine pigments, there has been a great need for a simplified manufacturing process.

The present invention is based on the unexpected observation that 2,5 - diacylamino-3,6 - dihalogeno - hydroquinones may be obtained in a simple manner by treating a 2,5 - diamino - 3,6 - dihalogeno - hydroquinone with an acylating agent in which operation, depending on the amount of acylating agents used, the desired 2,5-diacylamino-3,6 - dihalogeno - hydroquinone is obtained directly, or a tri-acyl or tetra-acyl-2,5-diamino-3,6-dihalogeno-hydroquinone is obtained and is hydrolysed to yield the 2,5-diacylamino-3,6-dihalogeno - hydroquinone. The 2,5 - diamino - 3,6 - dihalogeno - hydroquinone to

be used as starting material is advantageously prepared by reducing a 2,5-diamino-3,6-dihalogeno-benzoquinone, especially 2,5-diamino - 3,6 - dichloro - 1,4 - benzoquinone which itself is readily obtainable by reacting ammonia and tetrachloro - 1,4 - benzoquinone (chloranil). Suitable reducing agents for this purpose are all those whose reduction potential is sufficient to reduce benzoquinone to hydroquinone, for example, sulphur dioxide, sodium dithionite, iron and hydrochloric acid, zinc dust in pyridine or glacial acetic acid, stannous chloride, titanium trichloride, hydrazine, phenylhydrazine or hydroxylamine. Catalytic hydrogenation, for example, with Raney nickel as catalyst, is especially favourable.

Depending on the reducing agent chosen, the reduction may be carried out in an aqueous suspension or in an organic solvent or diluent, for example, chloroform, chlorobenzene, orthodichlorobenzene, glacial acetic acid, glycol monomethyl or dialkyl ether, dimethylformamide, N - methylpyrrolidone, ethyl acetate, N,N-dimethylacetamide or pyridine.

Since the resulting diamino-dihalogeno-hydroquinones are very sensitive towards oxidising agents, it is advantageous to isolate them in the form of their salts, especially the hydrochlorides, or to acylate them directly in the reaction mixture, especially when the reduction has been performed in an organic solvent with the use of a catalyst.

As acylating agents there may be mentioned the anhydrides and halides of aliphatic, cycloaliphatic or araliphatic carboxylic acids, for example, acetic anhydride, acetylchloride, propionylchloride, butyrylchloride, lauroylchloride, hexahydrobenzoylchloride, phenylacetylchloride, and more especially the anhydrides and halides of aromatic or heterocyclic carboxylic acids, especially benzoyl halides, for example, benzoylchloride, orthochlorobenzoylchloride, para - chlorobenzoyl-

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chloride, 2,4-dichlorobenzoylchloride, *o*-, *m*- or *p*-methoxybenzoylchloride, *p*-nitrobenzoylchloride, furthermore α - or β -naphthoylchloride, diphenyl-4-carboxylic acid chloride, pyridinecarboxylic acid chloride, furan-2-carboxylic acid chloride and thiophenecarboxylic acid chloride; also the chlorides of aliphatic or aromatic sulphonic acids, for example, methanesulphonylchloride, benzoylsulphonylchloride or para-toluylsulphonylchloride, chlorocarbonic acid esters, for example, the methyl or ethyl ester, phenylisocyanate and also halogenotriazines, for example, 2-chloro-4,6-diphenyl-1,3,5-triazine or 2-chloro-4,6-diphenoxy-1,3,5-triazine. The acylation is advantageously carried out at an elevated temperature. The acylation is advantageously carried out in an organic solvent, preferably pyridine. The resulting 2,5-diacylamino-3,6-dihalogenohydroquinones are advantageously isolated from the reaction vessel in the form of their hydrohalides.

When a large excess of acylating agent is used, there are obtained tri-acylated or tetra-acylated 2,5-diamino-3,6-dihalogenohydroquinones which can be converted into the 2,5-diacylamino-3,6-dihalogenohydroquinones by partial hydrolysis, for example, by treatment with an alkali, especially with sodium carbonate, or with an inorganic acid.

If mixed acylating agents are used, one being an aromatic acid derivative, the tri- or tetra-acyl derivatives produced yield di-acyl derivatives on partial hydrolysis irrespective of the nature of the other acylating agent.

For the conversion of the hydroquinones into the corresponding quinones an oxidant conventionally used for such reactions may be used, for example, lead dioxide, ferric chloride, chlorine, bromine, chromates, dichromates, chlorates, manganese dioxide, a permanganate or hydrogen peroxide. Nitric acid is especially suitable for this purpose.

The oxidation is advantageously carried out in an inert organic solvent, for example, in an aliphatic or aromatic hydrocarbon which may be halogenated, for example, benzene, chlorobenzene, chloroform, carbon tetrachloride, tetrachlorethane, nitrated hydrocarbons, for example, nitrobenzene or especially glacial acetic acid, advantageously at an elevated temperature.

The resulting diacylamino-dihalogenohydroquinones are easy to isolate from the reaction mixture by filtration.

The following Examples illustrate the invention. Unless otherwise indicated, parts and percentages in the following Examples are by weight.

EXAMPLE 1

A suspension of 20.7 parts of 2,5-diamino-3,6-dichloro-1,4-benzoquinone in 300 parts of glacial acetic acid is hydrogenated with

hydrogen at 25 to 35°C in the presence of Raney nickel. The reduction suspension, which contains the 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene, is heated to 50°C while being stirred in a flask with ground stopper. 14.9 Parts of benzoylchloride are dropped in during 10 minutes, and the temperature is raised within 30 minutes to 90°C and kept for 20 hours at 90 to 95°C. After cooling, the reaction mixture is filtered and washed with glacial acetic acid. The residue is crystallized directly from ortho-dichlorobenzene. The resulting 2,5-dibenzoylamino-3,6-dichloro-1,4-dihydroxybenzene decomposes at 265°C.

8 Parts of nitric acid of 65% strength in 10 parts of glacial acetic acid are vigorously stirred into a suspension of 8.35 parts of 2,5-dibenzoylamino-3,6-dichloro-1,4-dihydroxybenzene in 60 parts of glacial acetic acid. The temperature is raised within a short time to 70°C and then kept for 25 minutes at 50 to 60°C. The cooled batch is suctioned, washed with glacial acetic acid and the residue crystallized from ortho-dichlorobenzene. The deep yellow 2,5-dibenzoylamino-3,6-dichlorobenzoquinone-(1,4) decomposes at 265°C and reveals the following analytical data:

calculated:	C 57.85	H 2.91	Cl 17.08%
found:	57.69	2.75	17.04%

EXAMPLE 2

A suspension of 20.7 parts of 2,5-diamino-3,6-dichloro-1,4-benzoquinone in 140 parts of pyridine is hydrogenated with hydrogen at 25 to 35°C in the presence of Raney nickel. During 5 minutes, 35 parts of benzoylchloride are dropped into the reduction suspension, which contains the 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene, and the temperature is raised during 5 minutes to 90°C and the batch is stirred for one hour at this temperature, then cooled, and poured into 1200 parts of a 10% solution of hydrochloric acid. The precipitate formed is suctioned off and dissolved with heating in 2000 parts of sodium carbonate solution of 5% strength. The dark solution is filtered while still hot, cooled to room temperature and then poured into 2500 parts of a hydrochloric acid solution of 10% strength. The precipitated 2,5-dibenzoylamino-3,6-dichloro-1,4-dihydroxybenzene is suctioned off, washed until the washings run neutral and dried under vacuum at 70°C; it forms a powder of light beige colour which melts at 263°C.

EXAMPLE 3

A solution of 5.6 parts of 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene dihydrochloride in 30 parts of pyridine is mixed with 7 parts of benzoylchloride, heated to 90°C, stirred for one hour at this temperature, cooled to room temperature and then poured into 220 parts

of hydrochloric acid solution of 10% strength. The precipitate formed is suctioned off and dissolved with heating in 400 parts of sodium carbonate solution of 5% strength. The solution is filtered while still hot, cooled to room temperature and poured into 500 parts of a hydrochloric acid solution of 10% strength. The precipitate formed is suctioned off, washed until the washings run neutral and dried under vacuum at 70°C. The resulting 2,5-dibenzoylamino-3,6-dichloro-1,4-dihydroxybenzene melts at 260°C.

Instead of benzoylchloride it is possible to use 11.3 parts of benzoic anhydride in the above Example.

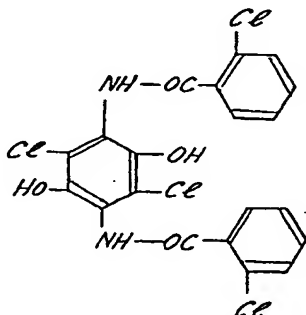
2,5-Diamino-3,6-dichloro-1,4-dihydroxybenzene dihydrochloride is prepared from a solution of 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene in hydrochloric acid of 7% strength by mixing it with concentrated hydrochloric acid. It forms a light grey powder which melts with decomposition between 240 and 270°C.

EXAMPLE 4

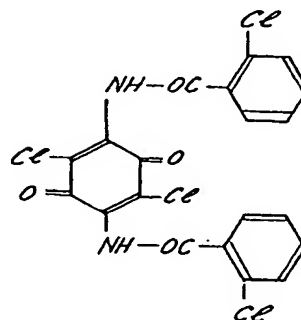
A suspension of 5.6 parts of 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene dihydrochloride in 30 parts of N,N-dimethylacetamide is mixed with 7 parts of benzoylchloride and then heated to 90°C. The resulting solution is stirred for 1 hour at 90°C, then cooled to room temperature and worked up as described in Example 3. The product thus obtained is 2,5-dibenzoylamino-3,6-dichloro-hydroquinone.

EXAMPLE 5

A solution of 5.6 parts of 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene dihydrochloride in 30 parts of pyridine is mixed with 8.75 parts of 2-chlorobenzoylchloride, heated to 90°C, stirred for 1 hour at this temperature, then cooled to room temperature and worked up as described in Example 3. The resulting product of the formula



forms a beige coloured powder which melts with decomposition at 256 to 257°C. Oxidation of this compound as described in Example 1 gives rise to the quinone of the formula

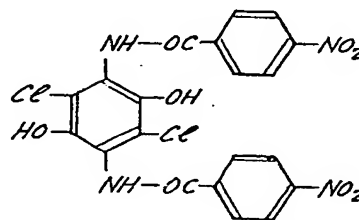


which forms a deep yellow powder melting at 266 to 269°C.

When 3-chloro-, 4-chloro- or 2,4-dichlorobenzoylchloride is used, the corresponding substituted 2,5-dibenzoylamino-3,6-dichloro-hydroquinones are obtained.

EXAMPLE 6

When 5.6 parts of 2,5-diamino-3,6-dichloro-1,4-dihydroxybenzene dihydrochloride are reacted with 9.3 parts of 4-nitrobenzoylchloride by the process described in Example 3, the compound of the formula

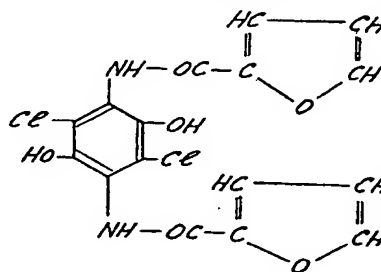


is obtained which melts at 250°C. The corresponding quinone melts at 261°C.

When 2-nitro- or 3-nitro-benzoylchloride is used, the corresponding substituted 2,5-dibenzoylamino-3,6-hydroquinones are obtained.

EXAMPLE 7

The compound of the formula

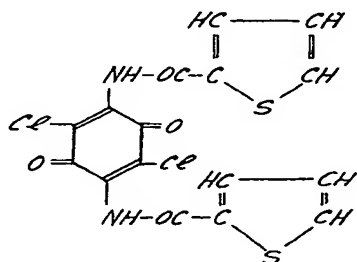


is prepared from 5.6 parts of 2,5-diamino-3,6-dichloro-hydroquinone dihydrochloride and 6.7 parts of furan-2-carboxylic acid

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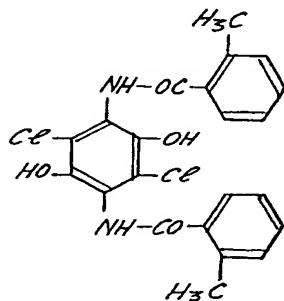
chloride by the method described in Example 3; it melts at 273 to 276°C, with the melt solidifying again at 282°C. The corresponding quinone melts at 282 to 284°C.

- 5 Equivalent results are obtained with 2-thiophenecarboxylic acid chloride instead of 2-furoylchloride, and in this case the product corresponds to the formula



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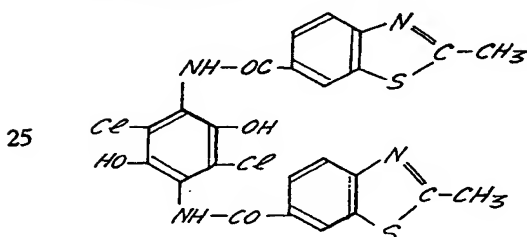
EXAMPLE 8
The compound of the formula



- 15 is obtained from 5.6 parts of 2,5-diamino-3,6-dichlorohydroquinone - dihydrochloride and 7.7 parts of ortho-toluychloride by the method described in Example 3; the compound melts at 251 to 255°C, the corresponding benzoquinone derivative at 264 to 266°C.

- 20 When ortho-toluychloride is replaced by meta- or para-toluychloride, 2,5-di-(meta- or para-methylbenzoylamino) - 3,6-dichlorohydroquinone is obtained.

EXAMPLE 9
The compound of the formula



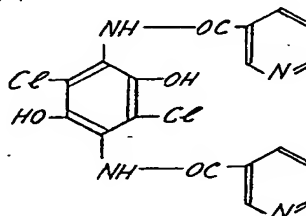
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is obtained from 5.6 parts of 2,5-diamino-3,6-dichlorohydroquinone dihydrochloride

and 10.6 parts of 2-methyl-benzthiazole-carboxylic acid chloride-(6) by the method described in Example 3. It melts above 320°C, and the corresponding benzoquinone above 350°C. 30

EXAMPLE 10

A solution of 5.6 parts of 2,5-diamino-3,6-dichlorohydroquinone dihydrochloride in 30 parts of pyridine is mixed with 7.1 parts of nicotinoylchloride, heated to 90°C, stirred for one hour at this temperature, then cooled to room temperature and poured into 440 parts of water. The resulting sticky suspension is left to stand for 19 hours and the product of the formula 35 40



which by then has solidified is suctioned off and dried. It melts at 225 to 228°C. 45

The oxidation furnishing the benzoquinone is carried out thus: 7.55 parts of the hydroquinone derivative of the above formula are suspended in 60 parts of glacial acetic acid, and 8 parts of nitric acid of 65% strength are vigorously stirred in. A dark brown solution forms, from which after a short time a yellow precipitate settles out. The suspension obtained in this manner is stirred for 3 hours at 30°C, then kept for 16 hours at room temperature and suctioned. The residue is finally washed with glacial acetic acid and petroleum ether. The product forms a matt yellow powder melting at 155°C with decomposition. 50 55

EXAMPLE 11

14.0 Parts of benzoylchloride are stirred at room temperature in a solution of 5.6 parts of 2,5-diamino-3,6-dichlorohydroquinone dihydrochloride in 30 parts of pyridine; the batch is heated to 90°C, stirred for one hour at 90°C and then cooled to room temperature. The precipitated thick suspension is poured into 220 parts of hydrochloric acid of 10% strength. The precipitate formed is suctioned off, washed until the washings run neutral and recrystallized from glacial acetic acid. The 2,5-dibenzoylamino-3,6-dichlorohydroquinone dibenzoate obtained in this manner melts at 275 to 276°C. 60 65 70

A suspension of 9.3 parts of 2,5-dibenzoylamino-3,6-dichlorohydroquinone dibenzoate in 400 parts of sodium carbonate solution of 5% strength is heated to 100°C and then stirred for 15 hours at this temperature. The resulting dark solution is filtered hot, cooled to room temperature and poured into 80

500 parts of a hydrochloric acid solution of 10% strength. The precipitate formed is suctioned off, washed until the washings run neutral and dried under vacuum at 70°C; it is identical with the substance prepared as described in Example 1.

EXAMPLE 12

8.2 Parts of benzoylchloride are stirred at room temperature into a solution of 5.6 parts of 2,5-diamino-3,6-dichlorohydroquinone dihydrochloride in 30 parts of pyridine, the whole is heated to 90°C, stirred for 1 hour at 90°C and then cooled to room temperature. The suspension formed is poured into 220 parts of hydrochloric acid of 10% strength. The precipitate thus obtained is suctioned off, washed until the washings run neutral and recrystallized from glacial acetic acid. The 2,5 - dibenzoylamino - 3,6 - dichloro - hydroquinone monobenzoate obtained in this manner melts at 244 to 246°C.

A suspension of 7.7 parts of 2,5-dibenzoylamino - 3,6 - dichloro - hydroquinone monobenzoate in 400 parts of sodium carbonate solution of 5% strength is heated to 100°C. The resulting dark solution is filtered hot, cooled to room temperature and poured into 500 parts of a hydrochloric acid solution of 10% strength. The precipitated 2,5-dibenzoylamino - 3,6 - dichloro - hydroquinone is then worked up as described in Example 11.

EXAMPLE 13

A suspension of 7.5 parts of 2,5-diacetylamino - 3,6 - dichloro - hydroquinone dibenzoate in 400 parts of sodium carbonate solution of 5% strength is heated to 100°C and then stirred at this temperature for 3 hours. A dark solution is obtained which is filtered hot, cooled to room temperature and poured into 500 parts of a hydrochloric acid solution of 10% strength. The precipitated 2,5 - dibenzoylamino - 3,6 - dichloro - hydroquinone is then worked up as described in Example 11. It melts at 267 to 268°C.

2,5 - Diacetylamino - 3,6 - dichloro-hydroquinone dibenzoate is obtained by condensing 1 mol of 2,5-diacetylamino-3,6-dichlorohydroquinone with 2 mols of benzoylchloride in pyridine. The product melts between 265 and 270°C.

WHAT WE CLAIM IS:—

1. A process for the manufacture of 2,5-diacetylamino - 3,6 - dihalogeno-hydroquinones, which comprises treating a 2,5-diamino-3,6-dihalogeno - hydroquinone with an acylating agent in which operation, depending on the amount of acylating agent used, the desired 2,5 - diacetylamino - 3,6 - dihalogeno - hydroquinone is obtained directly, or a tri-acyl or tetra - acyl - 2,5 - diamino - 3,6 - dihalogeno-hydroquinone is obtained and is hydrolysed to yield the 2,5 - diacetylamino - 3,6 - dihalogeno-hydroquinone.

2. A process as claimed in claim 1, wherein the starting material used is a 2,5-diamino-3,6-dichloro-hydroquinone.

3. A process as claimed in claim 1 or 2, wherein an anhydride or a halide of an aliphatic, cycloaliphatic, or araliphatic carboxylic acid is used as the acylating agent.

4. A process as claimed in claim 3, wherein the acylating agent is acetic anhydride, acetyl chloride, propionyl chloride, butyryl chloride, lauroyl chloride, hexahydrobenzoylchloride or phenylacetylchloride.

5. A process as claimed in claim 1 or 2, wherein the acylating agent used is an anhydride or halide of an aromatic or heterocyclic carboxylic acid.

6. A process as claimed in claim 5, wherein the acylating agent used is a benzoyl halide.

7. A process as claimed in claim 1 or 2, wherein the acylating agent used is a chloride of an aliphatic or aromatic sulphonic acid, a chlorocarbonic acid or a halogeno-triazine.

8. A process as claimed in any one of claims 1 to 7, wherein the acylation is carried out at an elevated temperature.

9. A process as claimed in any one of claims 1 to 8, wherein the acylation is carried out in an organic solvent.

10. A process as claimed in claim 9, wherein the organic solvent is pyridine.

11. A process as claimed in any one of claims 1 to 10, wherein 1 mol of a 2,5-diamino-3,6 - dihalogeno - hydroquinone is treated with more than two mols of a single acylating agent and the tri- or tetra-acylated 2,5-diamino-3,6-dihalogeno-hydroquinone obtained is partially hydrolysed by treatment with an alkali or with an inorganic acid.

12. A process as claimed in any one of claims 1 to 10, wherein 1 mol of a 2,5-diamino - 3,6 - dihalogeno - hydroquinone is first diacylated with an aliphatic acid derivative and the 2,5-dialkanoylamino-3,6-dihalogeno-hydroquinone so obtained is diacylated with an aromatic acid derivative, to yield the tetra-acylated 2,5 - diamino - 3,6 - dihalogeno - hydro - quinone which on partial hydrolysis yields the 2,5-diaroylamino-3,6-dihalogeno-hydroquinone.

13. A process as claimed in claim 11 or 12, wherein the partial hydrolysis is carried out with sodium carbonate.

14. A process for the manufacture of 2,5-diacetylamino - 3,6 - dihalogeno - 1,4 - benzoquinones, wherein a 2,5 - diamino - 3,6-dihalogeno-benzoquinone is reduced to the 2,5 - diamino - 3,6 - dihalogeno - 1,4 - hydroquinone, and the latter is treated with an acylating agent as claimed in claim 1 and the resulting diacetylamino hydroquinone is then oxidized to the 2,5-diacetylamino-3,6-dihalogeno-1,4-benzoquinone.

15. A process as claimed in claim 14, wherein the treatment with an acylating agent is as specified in any one of claims 3 to 13.

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16. A process as claimed in claim 14 or 15, wherein the starting material is a 2,5-diamino-3,6-dichlorobenzoquinone.
- 5 17. A process as claimed in any one of claims 14 to 16, wherein the oxidising agent used is nitric acid.
18. A process as claimed in any one of claims 14 to 16, wherein the oxidation is carried out in an inert organic solvent.
- 10 19. A process as claimed in claim 18, wherein the inert organic solvent is an aliphatic or aromatic hydrocarbon which may be halogenated, or a nitrated hydrocarbon.
- 15 20. A process as claimed in any one of claims 14 to 19, wherein the oxidation is carried out at an elevated temperature.
21. A process for the manufacture of 2,5-diacylamino - 3,6 - dihalogeno-hydroquinones conducted substantially as described in any one of the Examples herein. 20
22. 2,5 - Diacylamino - 3,6 - dihalogeno-hydroquinones whenever prepared by the process claimed in any one of claims 1 to 13.
23. A process for the manufacture of 2,5-diacylamino - 3,6 - dihalogenobenzoquinones conducted substantially as described in any one of the Examples herein. 25
24. 2,5 - Diacylamino - 3,6 - dihalogenobenzoquinones whenever prepared by the process claimed in any one of claims 14 to 20. 30

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